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(57) Abstract

This invention provides a method of making single-wall carbon nanotubes by laser vaporizing a mixture of carbon and one or more Group VIII transition metals. Single-wall carbon nanotubes preferentially form in the vapor and the one or more Group VIII transition metals catalyzed growth of the single-wall carbon nanotubes. In one embodiment of the invention, one or more single-wall carbon nanotubes are fixed in a high temperature zone so that the one or more Group VIII transition metals catalyze further growth of the single-wall carbon nanotube that is maintained in the high temperature zone. In another embodiment, two separate laser pulses are utilized with the second pulse timed to be absorbed by the vapor created by the first pulse.

passed through the tube and the pressure in the tube maintained at about 500 Torr. Material from one end of the graphite/transition-metal composite rod was vaporized with a laser to form a vapor comprising carbon, cobalt and nickel. The soot collected from that vapor produced single-wall carbon nanotubes in concentrations much greater than observed before. About 50% or more of all of the carbon in the deposits of product collected downstream of the composite rod were single-wall carbon nanotubes present either as individual nanotubes or as ropes of nanotubes. Other combinations of two or more Group VIII transition metals as well as any Group VIII transition metal used singularly will produce the single-wall carbon nanotubes in the method of this invention, at concentrations of 0.1 to 10 atom %. Preferably, one or more Group VIII transition metals selected from the group of ruthenium, cobalt, nickel and platinum are used.

The invention also includes an embodiment where carbon nanotubes having a live end, preferably single-wall carbon nanotubes, are caught and maintained in the heated portion of the tube (annealing zone). A tungsten wire or mesh grid may be mounted in the tube downstream of the target to catch some of the carbon nanotubes formed from vaporization of the target comprising carbon and one or more Group VIII transition metals. After the carbon nanotube having a live end is caught, the carbon vapor supplied to the live end of the carbon nanotube may be supplied by: (i) continued laser vaporization of the target comprising carbon and one or more Group VIII transition metals; (ii) stopping laser vaporization of the target comprising carbon and one or more Group VIII transition metals and starting laser vaporization of a target comprising, consisting essentially of or consisting of carbon, (iii) stopping laser vaporization altogether and introducing carbon to the live end of the carbon nanotube from some other source. Step (iii) may be accomplished, for example, by adding graphite particles, fullerene particles, carbon vapor, carbon monoxide (CO), or hydrocarbons to the argon gas flowing past the live end of the carbon nanotube or by flowing CO or a hydrocarbon gas (without using an inert gas) past the live end of the carbon nanotube. In this embodiment,

a "wall" of the carbon nanotube. In theory, there is no limit to the number of walls possible on a carbon nanotube, and carbon nanotubes having up to seven walls have been recognized in the prior art. Ebbesen II; Iijima et al., "Helical Microtubules Of Graphitic Carbon," *Nature*, Vol. 354, p. 56 (November 7, 1991).

Multi-wall carbon nanotubes have been discovered in carbon deposits on carbon electrodes that have been used in carbon arc methods of making fullerenes. Ebbesen I; Ebbesen II. It is also known that single-wall carbon nanotubes can be made by adding a specific metal or a mixture of specific metals to the carbon in one or both of the carbon electrodes used in a carbon arc apparatus for making fullerenes. See Iijima et al., "Single-Shell Carbon Nanotubes of 1 nm Diameter," *Nature*, Vol. 363, p. 603 (1993); and Bethune et al., "Cobalt Catalyzed Growth of Carbon Nanotubes with Single Atomic Layer Walls," *Nature*, Vol. 363, p. 605 (1993). The prior art recognized a method of making single-wall carbon nanotubes using a DC arc discharge apparatus previously known to be useful in making fullerenes described by U.S. Patent No. 5,227,038. Single-wall carbon nanotubes were made using the DC arc discharge apparatus by simultaneously evaporating carbon and a small percentage of Group VIII transition metal from the anode of the arc discharge apparatus. See Iijima et al., "Single-Shell Carbon Nanotubes of 1 nm Diameter," *Nature*, Vol. 363, p. 603 (1993); Bethune et al., "Cobalt Catalyzed Growth of Carbon Nanotubes with Single Atomic Layer Walls," *Nature*, Vol. 63, p. 605 (1993); Ajayan et al., "Growth Morphologies During Cobalt Catalyzed Single-Shell Carbon Nanotube Synthesis," *Chem. Phys. Lett.*, Vol. 215, p. 509 (1993); Zhou et al., "Single-Walled Carbon Nanotubes Growing Radially From YC_2 Particles," *Appl. Phys. Lett.*, Vol. 65, p. 1593 (1994); Seraphin et al., "Single-Walled Tubes and Encapsulation of Nanocrystals Into Carbon Clusters," *Electrochem. Soc.*, Vol. 142, p. 290 (1995); Saito et al., "Carbon Nanocapsules Encaging Metals and Carbides," *J. Phys. Chem. Solids*, Vol. 54, p. 1849 (1993); Saito et al., "Extrusion of Single-Wall Carbon Nanotubes Via Formation of Small Particles Condensed Near an Evaporation Source," *Chem.*

supports for catalysts used in industrial and chemical processes such as hydrogenation, reforming and cracking catalysts.

Ropes of single-wall carbon nanotubes made by this invention are metallic, i.e., they will conduct electrical charges with a relatively low resistance. Ropes are useful in any application where an electrical conductor is needed, for example as an additive in electrically conductive points or in polymer coatings or as the probing tip of an STM or AFM.

In defining carbon nanotubes, it is helpful to use a recognized system of nomenclature. In this application, the carbon nanotube nomenclature described by M.S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerness and Carbon Nanotubes*, Chap. 19, especially pp. 756-760, (1996), published by Academic Press, 525 B Street, Suite 1900, San Diego, California 92101-4495 or 6277 Sea Harbor Drive, Orlando, Florida 32877 (ISBN 0-12-221820-5), which is hereby incorporated by reference, will be used. The dual laser pulse feature described herein produces an abundance of (10,10) single-wall carbon nanotubes. The (10, 10) tubes are known as "armchair" tubes. All armchair tubes are metallic. Other armchair tubes are denoted as (n, n) where n is an integer from 1 to infinity, preferably 1 to 1000 more preferably 5 to 500. The (10,10), single-wall carbon nanotubes have an approximate tube diameter of 13.8 Å ± 0.3 Å or 13.8 Å ± 0.2 Å.

The present invention provides a method for making single-wall carbon nanotubes in which a laser beam vaporizes material from a target comprising, consisting essentially of, or consisting of a mixture of carbon and one or more Group VIII transition metals. The vapor from the target forms carbon nanotubes that are predominantly single-wall carbon nanotubes, and of those, the (10, 10) tube is predominant. The method also produces significant amounts of single-wall carbon nanotubes that are arranged as ropes, i.e., the single-wall carbon nanotubes run parallel to each other as shown by Figures 2A-2E. Again, the (10, 10) tube is the predominant tube found in each rope. The laser vaporization method provides several advantages over the arc discharge method of making carbon

One aspect of the invention comprises a method of making carbon nanotubes and/or ropes of carbon nanotubes which comprises supplying carbon vapor to the live end of a carbon nanotube while maintaining the live end of a carbon nanotube in an annealing zone. Carbon can be vaporized in accordance with this invention by an apparatus in which a laser beam impinges on a target comprising carbon that is maintained in a heated zone. A similar apparatus has been described in the literature, for example, in U.S. Patent No. 5,300,203 which is incorporated herein by reference, and in Chai, et al., "Fullerenes with Metals Inside," *J. Phys. Chem.*, vol. 95, no. 20, p. 7564 (1991).

Carbon nanotubes having at least one live end are formed when the target also comprises a Group VIII transition metal or mixtures of two or more Group VIII transition metals. In this application, the term "live end" of a carbon nanotube refers to the end of the carbon nanotube on which atoms of the one or more Group VIII transition metals are located. One or both ends of the nanotube may be a live end. A carbon nanotube having a live end is initially produced in the laser vaporization apparatus of this invention by using a laser beam to vaporize material from a target comprising carbon and one or more Group VIII transition metals and then introducing the carbon/Group VIII transition metal vapor to an annealing zone. Optionally, a second laser beam is used to assist in vaporizing carbon from the target. A carbon nanotube having a live end will form in the annealing zone and then grow in length by the catalytic addition of carbon from the vapor to the live end of the carbon nanotube. Additional carbon vapor is then supplied to the live end of a carbon nanotube to increase the length of the carbon nanotube.

The carbon nanotube that is formed is not always a single-wall carbon nanotube; it may be a multi-wall carbon nanotubes having two, five, ten or any greater number of walls (concentric carbon nanotubes). Preferably, though, the carbon nanotube is a single-wall carbon nanotube and this invention provides a way

presence of too much water (H_2O) and/or oxygen (O_2) will kill or significantly decrease the catalytic activity of the one or more Group VIII transition metals. Therefore, water and oxygen are preferably excluded from the atmosphere in the annealing zone. Ordinarily, the use of a sweep gas having less than 5 wt%, more preferably less than 1 wt% water and oxygen will be sufficient. Most preferably the water and oxygen will be less than 0.1 wt%.

Preferably, the formation of the carbon nanotube having a live end and the subsequent addition of carbon vapor to the carbon nanotube are all accomplished in the same apparatus. Preferably, the apparatus comprises a laser that is aimed at a target comprising carbon and one or more Group VIII transition metals, and the target and the annealing zone are maintained at the appropriate temperature, for example by maintaining the annealing zone in an oven. A laser beam may be aimed to impinge on a target comprising carbon and one or more Group VIII transition metals where the target is mounted inside a quartz tube that is in turn maintained within a furnace maintained at the appropriate temperature. As noted above, the oven temperature is most preferably within the range of 1100° to 1300°C. The tube need not necessarily be a quartz tube; it may be made from any material that can withstand the temperatures (1000° to 1500°C.). Alumina or tungsten could be used to make the tube in addition to quartz.

Improved results are obtained where a second laser is also aimed at the target and both lasers are timed to deliver pulses of laser energy at separate times. For example, the first laser may deliver a pulse intense enough to vaporize material from the surface of the target. Typically, the pulse from the first laser will last about 10 nanoseconds (ns). After the first pulse has stopped, a pulse from a second laser hits the target or the carbon vapor or plasma created by the first pulse to provide more uniform and continued vaporization of material from the surface of the target. The second laser pulse may be the same intensity as the first pulse, or less intense, but the pulse from the second laser is typically more intense than the

small molecules (less than ten carbon atoms per molecule). If the second laser pulse arrives too soon after the first pulse, the plasma created by the first pulse may be so dense that the second laser pulse is reflected by the plasma. If the second laser pulse arrives too late after the first pulse, the plasma and/or ablated material created by the first laser pulse will strike the surface of the target. But if the second laser pulse is timed to arrive just after the plasma and/or ablated material has been formed, as described herein, then the plasma and/or ablated material will absorb energy from the second laser pulse. Also, it should be noted that the sequence of a first laser pulse followed by a second laser pulse will be repeated at the same repetition frequency as the first and second laser pulses, i.e., 0.01 to 1000 Hz.

In addition to lasers described in the Examples, other examples of lasers useful in this invention include an XeF (365 nm wavelength) laser, an XeCl (308 nm wavelength) laser, a KrF (248 nm wavelength) laser or an ArF (193 nm wavelength) laser.

Optionally but preferably a sweep gas is introduced to the tube upstream of the target and flows past the target carrying vapor from the target downstream. The quartz tube should be maintained at conditions so that the carbon vapor and the one or more Group VIII transition metals will form carbon nanotubes at a point downstream of the carbon target but still within the heated portion of the quartz tube. Collection of the carbon nanotubes that form in the annealing zone may be facilitated by maintaining a cooled collector in the internal portion of the far downstream end of the quartz tube. For example, carbon nanotubes may be collected on a water cooled metal structure mounted in the center of the quartz tube. The carbon nanotubes will collect where the conditions are appropriate, preferably on the water cooled collector.

Any Group VIII transition metal may be used as the one or more Group VIII transition metals in this invention. Group VIII transition metals are iron (Fe), cobalt (Co), nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), Iridium (Ir) and platinum (Pt). Preferably, the one or more

metals. The target may be made by uniformly mixing carbon and the one or more Group VIII transition metals with carbon cement at room temperature and then placing the mixture in a mold. The mixture in the mold is then compressed and heated to about 130°C. for about 4 or 5 hours while the epoxy resin of the carbon cement cures. The compression pressure used should be sufficient to compress the mixture of graphite, one or more Group VIII transition metals and carbon cement into a molded form that does not have voids so that the molded form will maintain structural integrity. The molded form is then carbonized by slowly heating it to a temperature of 810°C. for about 8 hours under an atmosphere of flowing argon. The molded and carbonized targets are then heated to about 1200°C. under flowing argon for about 12 hours prior to their use as a target to generate a vapor comprising carbon and the one or more Group VIII transition metals.

The invention may be further understood by reference to Figure 1 which is a cross-section view of laser vaporization in an oven. A target 10 is positioned within tube 12. The target 10 will comprise carbon and may comprise one or more Group VIII transition metals. Tube 12 is positioned in oven 14 which comprises insulation 16 and heating element zone 18. Corresponding portions of oven 14 are represented by insulation 16' and heating element zone 18'. Tube 12 is positioned in oven 14 so that target 10 is within heating element zone 18.

Figure 1 also shows water cooled collector 20 mounted inside tube 12 at the downstream end 24 of tube 12. An inert gas such as argon or helium may be introduced to the upstream end 22 of tube 12 so that flow is from the upstream end 22 of tube 12 to the downstream end 24. A laser beam 26 is produced by a laser (not shown) focused on target 10. In operation, oven 14 is heated to the desired temperature, preferably 1100° to 1300°C., usually about 1200°C. Argon is introduced to the upstream end 22 as a sweep gas. The argon may optionally be preheated to a desired temperature, which should be about the same as the temperature of oven 14. Laser beam 26 strikes target 10 vaporizing material in target 10. Vapor from target 10 is carried toward the downstream

Figure 3 shows an optional embodiment of the invention that can be used to make longer carbon nanotubes wherein a tungsten wire 32 is stretched across the diameter of tube 12 downstream of target 10 but still within the annealing zone. After laser beam pulses hit the target 10 forming a carbon/ Group VIII transition metal vapor, carbon nanotubes having live ends will form in the vapor. Some of those carbon nanotubes will be caught on the tungsten wire and the live end will be aimed toward the downstream end 24 of tube 12. Additional carbon vapor will make the carbon nanotube grow. Carbon nanotubes as long as the annealing zone of the apparatus can be made in this embodiment. In this embodiment, it is possible to switch to an all carbon target after initial formation of the carbon nanotubes having a live end, because the vapor need only contain carbon at that point.

Figure 3 also shows part of second laser beam 34 as it impacts on target 10. In practice, laser beam 26 and second laser beam 34 would be aimed at the same surface of target 10, but they would impact that surface at different times as described herein.

It is also possible to stop the laser or lasers altogether. Once the single-wall carbon nanotube having a live end is formed, the live end will catalyze growth of the single-wall carbon nanotube at lower temperatures and with other carbon sources. The carbon source can be switched to fullerenes, that can be transported to the live end by the flowing sweep gas. The carbon source can be graphite particles carried to the live end by the sweep gas. The carbon source can be a hydrocarbon that is carried to the live end by a sweep gas or a hydrocarbon gas or mixture of hydrocarbon gasses introduced to tube 12 to flow past the live end. Hydrocarbons useful include methane, ethane, propane, butane, ethylene, propylene, benzene, toluene or any other paraffinic, olefinic, cyclic or aromatic hydrocarbon, or any other hydrocarbon.

The annealing zone temperature in this embodiment can be lower than the annealing zone temperatures necessary to initially form the single-wall

was vaporized and subsequently deposited onto a water-cooled collector, made from copper, that was positioned downstream just outside the furnace.

Targets were uniformly mixed composite rods made by the following three-step procedure: (i) the paste produced from mixing high-purity metals or metal oxides at the ratios given below with graphite powder supplied by Carbone of America and carbon cement supplied by Dylon at room temperature was placed in a 0.5 inch diameter cylindrical mold, (ii) the mold containing the paste was placed in a hydraulic press equipped with heating plates, supplied by Carvey, and baked at 130°C. for 4 to 5 hours under constant pressure, and (iii) the baked rod (formed from the cylindrical mold) was then cured at 810°C. for 8 hours under an atmosphere of flowing argon. For each test, fresh targets were heated at 1200°C. under flowing argon for varying lengths of time, typically 12 hours, and subsequent runs with the same targets proceeded after 2 additional hours heating at 1200°C.

The following metal concentrations were used in this example: cobalt (1.0 atom per cent), copper (0.6 atom per cent), niobium (0.6 atom per cent), nickel (0.6 atom per cent), platinum (0.2 atom per cent), a mixture of cobalt and nickel (0.6 atom per cent/0.6 atom per cent respectively), a mixture of cobalt and platinum (0.6 atom per cent/0.2 atom per cent respectively), a mixture of cobalt and copper (0.6 atom per cent/0.5 atom per cent respectively), and a mixture of nickel and platinum (0.6 atom per cent/0.2 atom per cent respectively). The remainder of the mixture was primarily graphite along with small amounts of carbon cement. Each target was vaporized with a laser beam and the soots collected from the water cooled collector were then collected separately and processed by sonicating the soot for 1 hour in a solution of methanol at room temperature and pressure (other useful solvents include acetone, 1,2-dicholoroethane, 1-bromo, 1,2-dichloroethane, and N,N-dimethylformamide). With one exception, the products collected produced a homogeneous suspension after 30 to 60 minutes of sonication in methanol. One sample vaporized from a mixture of cobalt, nickel and graphite was a rubbery deposit having a small portion that did not fully disperse even after 2 hours of

The images shown in Figures 2A through 2E are transmission electron micrographs of single-wall carbon nanotubes produced by vaporizing a target comprising graphite and a mixture of cobalt and nickel (0.6 atom per cent/0.6 atom per cent respectively) at an oven temperature of 1200°C. Figure 2A shows a medium-magnification view (where the scale bar represents 100 mm) showing that almost everywhere, bundles of single-wall carbon nanotubes are tangled together with other single-wall carbon nanotubes. Figure 2B is a high-magnification image of one bundle of multiple single-wall carbon nanotubes that are all roughly parallel to each other. The single-wall carbon nanotubes all have a diameter of about 1 nm, with similar spacing between adjacent single-wall carbon nanotubes. The single-wall carbon nanotubes adhere to one another by van der Waals forces.

Figure 2C shows several overlapping bundles of single-wall carbon nanotubes, again showing the generally parallel nature of each single-wall nanotube with other single-wall carbon nanotubes in the same bundle, and showing the overlapping and bending nature of the various bundles of single-wall carbon nanotubes. Figure 2D shows several different bundles of single-wall carbon nanotubes, all of which are bent at various angles or arcs. One of the bends in the bundles is relatively sharp, illustrating the strength and flexibility of the bundle of single-wall carbon nanotubes. Figure 2E shows a cross-sectional view of a bundle of 7 single-wall carbon nanotubes, each running roughly parallel to the others. All of the transmission electron micrographs in Figures 2A through 2E clearly illustrate the lack of amorphous carbon overcoating that is typically seen in carbon nanotubes and single-wall carbon nanotubes grown in arc-discharge methods. The images in Figures 2A through 2E also reveal that the vast majority of the deposit comprises single-wall carbon nanotubes. The yield of single-wall carbon nanotubes is estimated to be about 50% of the carbon vaporized. The remaining 50% consists primarily of fullerenes, multi-layer fullerenes (fullerene onions) and/or amorphous carbon.

target being vaporized). Argon at 500 Torr. was passed through the quartz tube at a flow rate equivalent to a linear velocity in the quartz tube of about 1 cm/sec. The oven was maintained at 1200°C. and Group VIII transition metals were combined at 1 to 3 atom% with carbon to make the target.

The pulsed laser was operated as in Example 1 for 10 to 20 minutes. Eventually, a tear drop shaped deposit formed on the tungsten wire, with portions growing to lengths of 3 to 5 mm. The deposit resembled eyelashes growing on the tungsten wire. Examination of the deposit revealed bundles of millions of single-wall carbon nanotubes.

EXAMPLE 3

Graphite rods were prepared as described in Example 1 using graphite, graphite cement and 1.2 atom % of a mixture of 50 atom % cobalt powder and 50 atom % nickel powder. The graphite rods were pressed into shape and then formed into targets as described in Example 1. The graphite rods were then installed as targets in an apparatus as diagramed in Figure 3, except tungsten wire 32 was not used. A quartz tube holding the graphite rod targets was placed in an oven heated to 1200° C. Argon gas which had been catalytically purified to remove water vapor and oxygen was passed through the quartz tube at a pressure of about 500 Torr and a flow rate of about 50 sccm although flow rates in the range of about 1 to 500 sccm (standard cubic centimeters per minute), preferably 10 to 100 sccm are also useful for a 1 inch diameter flow tube. The first laser was set to deliver a 0.532 micron wavelength pulsed beam at 250 mJ per pulse. The pulse rate was 10 Hz and the pulse duration was 5 to 10 ns. A second laser pulse struck the target 50 ns after the end of the first pulse. The second laser was set to deliver a 1.064 micron wavelength pulsed beam at 300 mJ per pulse. The pulse rate was 10 Hz and the pulse duration was 5 to 10 ns. The first laser was focused to a 5 mm diameter spot on the target and the second laser was focused to a 7 mm diameter gaussian spot having the same center point on the target as the spot from the first laser. About 1/10th of a second after the second laser hit the target, the first and

75%, and even greater than 90% (10, 10) single-wall carbon nanotubes have been produced. Ropes having greater than 50% greater than 75% and greater than 90% armchair (n, n) single-wall carbon nanotubes are also made by and are a part of this invention. The single-wall carbon nanotubes in each rope are arranged to form a rope having a 2-D triangular lattice having a lattice constant of about 17Å. Ropes of 0.1 up to 10, 100 or 1,000 microns in length are made by the invention. The resistivity of a rope made in accordance with this invention was measured to be 0.34 to 1.0 micro ohms per meter at 27° C. proving that the ropes are metallic.

The invention also produces a "felt" of the ropes described above. The product material is collected as a tangled collection of ropes stuck together in a mat referred to herein as a "felt." The felt material collected from the inventive process has enough strength to withstand handling, and it has been measured to be electrically conductive. Felts of 10 mm^2, 100 mm^2, 1000 mm^2 or greater, are formed in the inventive process.

One advantage of the single-wall carbon nanotubes produced with the laser vaporization in an oven method is their cleanliness. Typical discharge arc-produced single-wall carbon nanotubes are covered with a thick layer of amorphous carbon, perhaps limiting their usefulness compared to the clean bundles of single-wall carbon nanotubes produced by the laser vaporization method. Other advantages and features of the invention are apparent from the disclosure. The invention may also be understood by reference to Guo et al., "Catalytic Growth Of Single-Walled Nanotubes By Laser Vaporization," *Chem. Phys. Lett.*, Vol. 243, pp. 49-54 (1995) and the provisional patent applications referenced at the beginning of this disclosure.

The advantages achieved by the dual pulsed lasers insure that the carbon and metal go through the optimum annealing conditions. The dual laser pulse process achieves this by using time to separate the ablation from the further and full vaporization of the ablated material. These same optimum conditions can be achieved by using solar energy to vaporize carbon and metals as described in

CLAIMS

1. A method of making single-wall carbon nanotubes which comprises:

(a) making a vapor comprising carbon and one or more Group VIII transition metals by vaporizing a mixture of carbon and one or more Group VIII transition metals with a first laser pulse;

(b) then condensing the vapor to form a single-wall carbon nanotube having a live end;

(c) then supplying carbon vapor to the line end of the single-wall carbon nanotube while maintaining the live end of the single-wall carbon nanotube in an annealing zone.

2. A method in accordance with claim 1 wherein the one or more Group VIII transition metals are selected from the group consisting of cobalt, ruthenium, nickel and platinum.

3. A method in accordance with claim 3 wherein the annealing zone is maintained at a temperature of 1000° to 1400°C and pressure of 100 to 800 Torr.

4. A method in accordance with claim 3 wherein the annealing zone atmosphere comprises carbon and a gas selected from the group of argon, neon, helium, carbon monoxide, and mixtures thereof.

5. A method in accordance with claim 4 wherein the annealing zone atmosphere consists essentially of carbon, one or more transition metals selected from the group consisting of iron, cobalt, ruthenium, nickel and platinum and a gas selected from the group of argon, neon, helium, carbon monoxide, and mixtures thereof.

6. A method in accordance with claim 1 wherein the step of making a vapor comprising carbon and one or more Group VIII transition metals further comprises a second laser pulse timed to arrive after the finish of the first pulse and before the vapor made by the first laser pulse has dissipated and focused so that the energy from the second laser pulse is absorbed by the vapor.

7. A method of making single-wall carbon nanotubes which comprises:

14. A method in accordance with claim 13 wherein the target further comprises one or more Group VIII transition metals.

15. A method in accordance with claim 14 wherein the one or more Group VIII transition metals are selected from the group consisting of iron, cobalt, ruthenium, nickel, and platinum.

16. A method in accordance with claim 15 wherein the vapor is condensed to form single-wall carbon nanotubes having a live end.

17. A method in accordance with claim 16 which further comprises maintaining the live end of the single-wall carbon nanotube in an annealing zone and supplying carbon vapor to the live end of the single-wall carbon nanotube.

18. A method in accordance with claim 17 wherein the target comprises 0.1 to 10 atom percent of one or more Group VIII transition metals selected from the group consisting of iron, cobalt, ruthenium, nickel, and platinum.

19. A method in accordance with claim 18 wherein the annealing zone is maintained at a temperature of from about 1000°C. to about 1400°C., and the pressure in the annealing zone is maintained at about 100 to about 800 Torr.

20. A method in accordance with claim 19 wherein the annealing zone is maintained in an atmosphere comprising carbon, and a gas selected from the group of argon, neon, helium, carbon monoxide and mixtures thereof.

21. A method in accordance with claim 19 wherein the delay is from about 40 ns to about 50 ns.

22. A single-wall carbon nanotube product made in accordance with any of the methods of claims 12, 13, 14, 15, 19 or 21.

23. A rope of single-wall carbon nanotubes having 50 to 5000 single-wall carbon nanotubes of which greater than 10% are (10, 10) single-wall carbon nanotubes.

24. A rope of single-wall carbon nanotubes in accordance with claim 23 wherein more than 50% are (10, 10) single-wall carbon nanotubes.

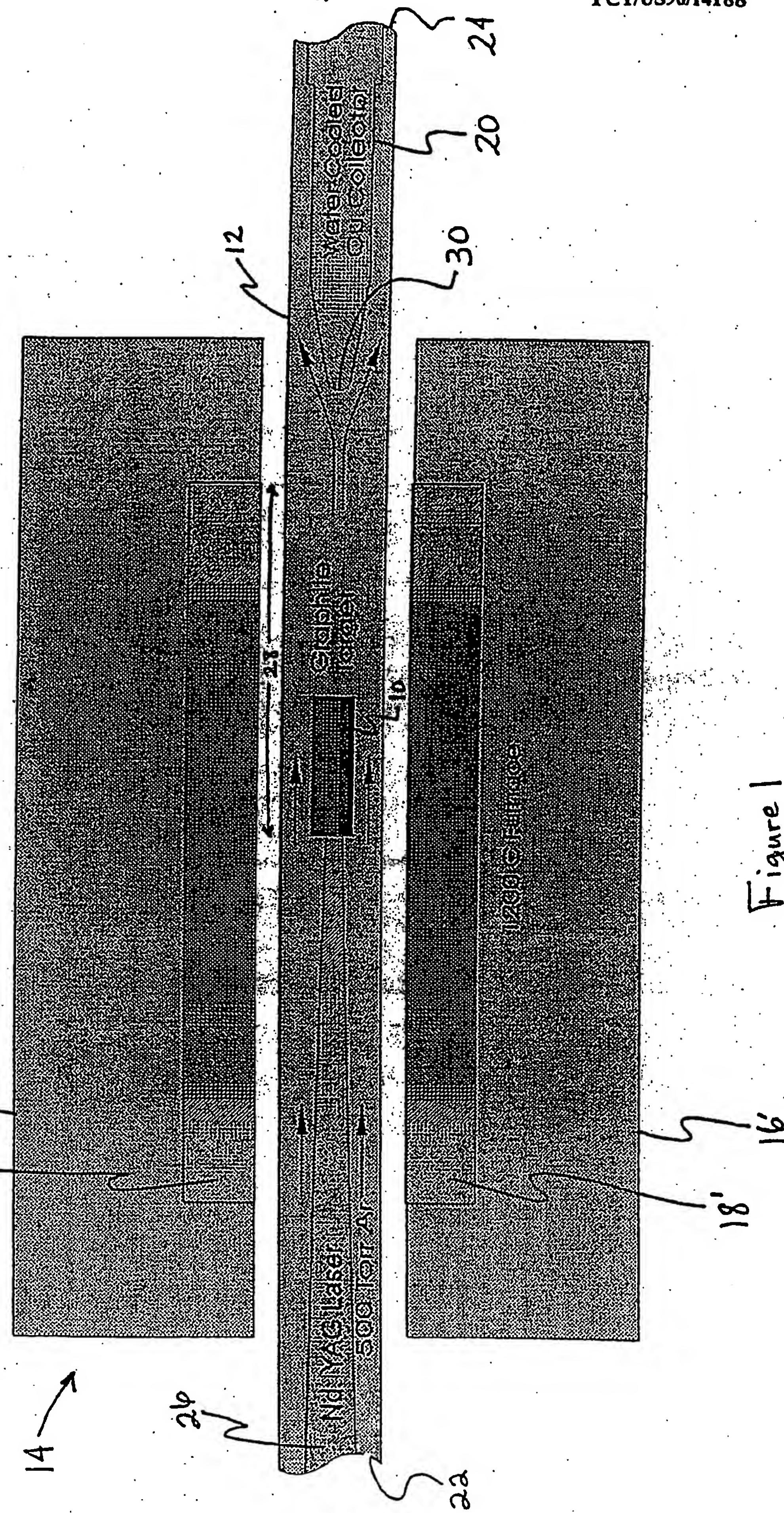
Water-cooled
Cu Collector
Graphite
Target
1200 °C Furnace
Nd:YAG Laser
500 Torr Ar
24
20
30
12
28
10
16
18
16'
18'
26
22
14

Figure 1

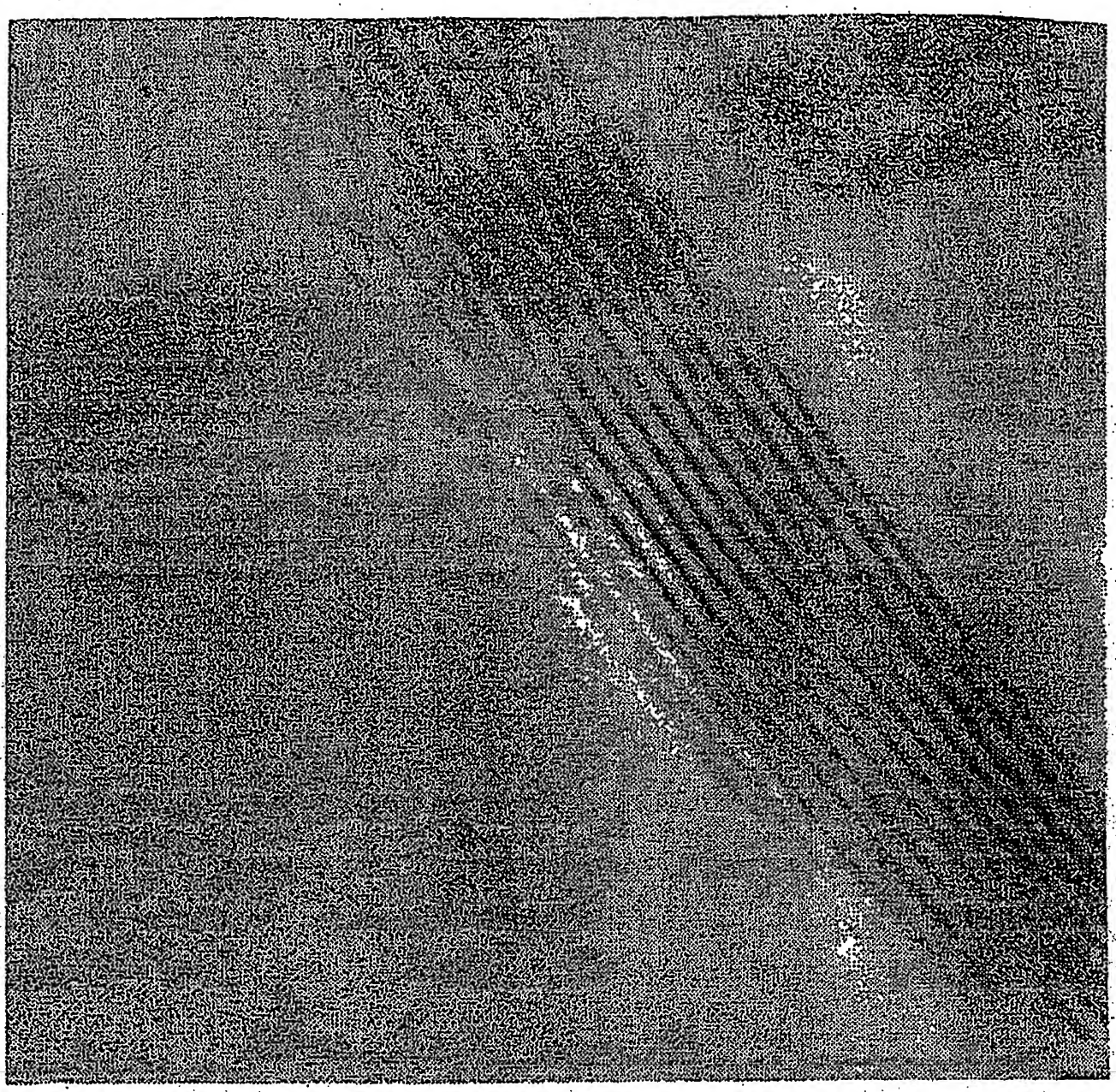

Figure 2B

Figure 2D

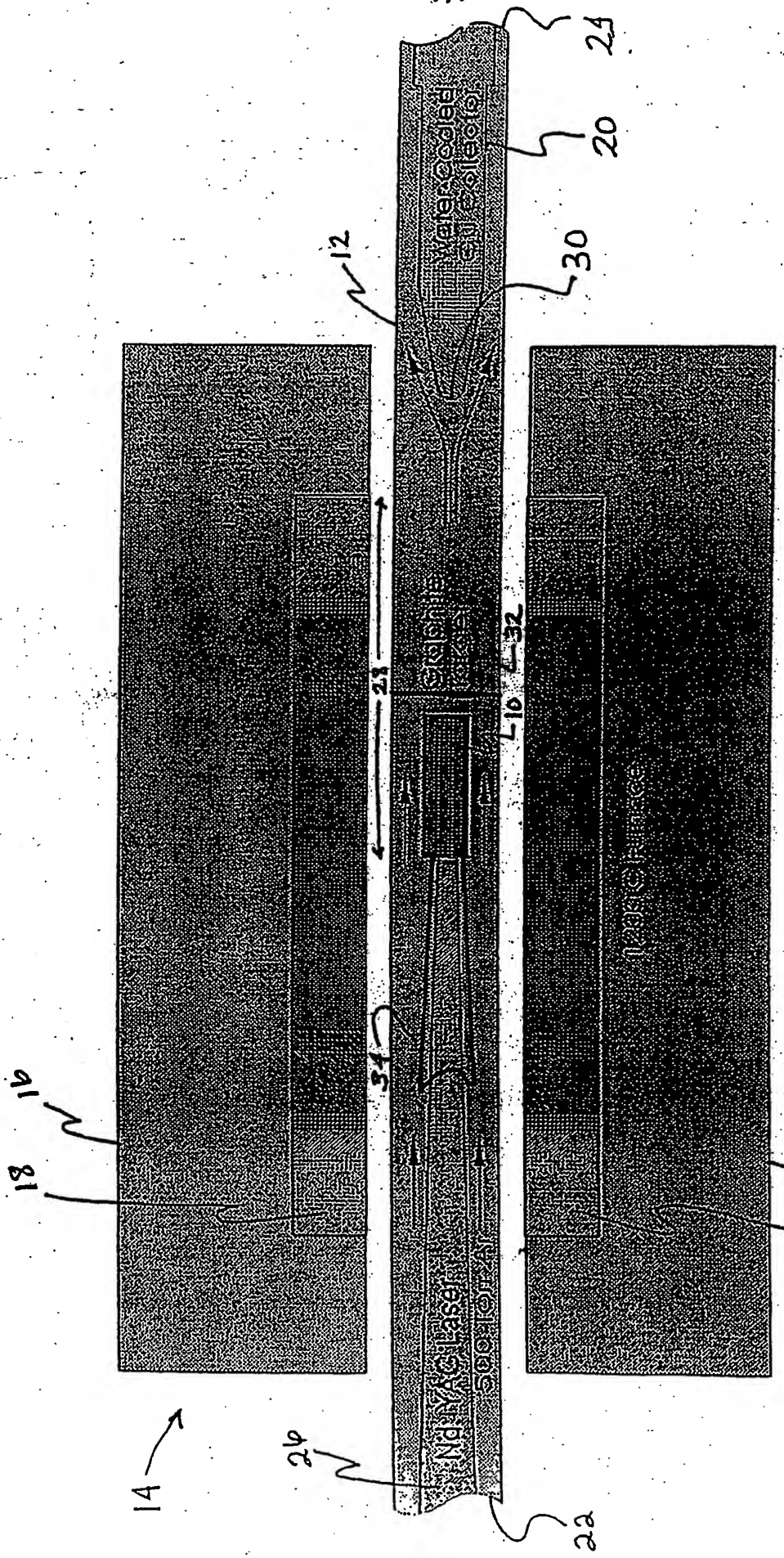

Figure3

INTERNATIONAL SEARCH REPORT

Intern. al Application No
PCT/US 96/14188

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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information on patent family members

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US-A-5300203	05-04-94	NONE	